

## Theoretical studies on quinones I. The structure of *p*-benzoquinone and two of its excited triplet states

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*Ab initio* calculations on the ground and two excited triplet states ( ${}^3B_{1g}$  and  ${}^3B_{1u}$ ) of *p*-benzoquinone are described. The geometries of the three states were fully optimised at the SCF level using the 3-21G basis set. For the excited states, both  $D_{2h}$  and  $C_{2v}$  geometries were investigated. Comparison was made between UHF and ROHF levels of theory.

**Key words:** *p*-Benzoquinone — Triplet — Geometry — Optimisation — *Ab initio*

### 1. Introduction

It has been known for many years that cigarette smoke and cigarette tar contain high concentrations of free radicals. The free radical in cigarette tar was originally suggested to be an odd electron delocalised over a polynuclear hydrocarbon molecule [1], probably a cation radical.

Pryor et al. [2] have, however, recently shown that there are in fact at least four paramagnetic species in tar, three of which are present at low concentrations, while the fourth with which we are concerned here is by far the predominant species. This species is not a monoradical, but a complex between quinone and hydroquinone groups in a polymeric matrix.

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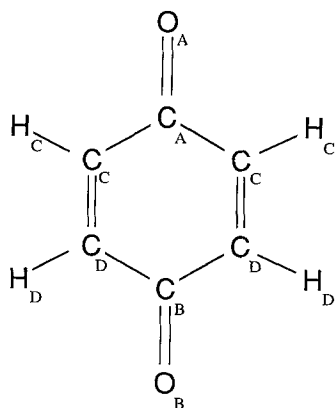


Fig. 1. *p*-benzoquinone: the labelling of the molecule

This article is the first in a series investigating this species with theoretical methods, and in the present study we report the geometries of the ground and two excited states of *p*-benzoquinone by *ab initio* self-consistent field techniques.

## 2. Method of calculation

The calculations were performed using the GAUSSIAN (80 [3] and 82 [4]) and GAMESS [5] systems of programs on the VAX 11/780 computers at St Andrews University and the CDC CYBER 205 at the University of Manchester Regional Computer Centre respectively. The wavefunction for the ground state was calculated using the restricted Hartree Fock (RHF) method [6], while for the excited triplet states a comparison was made between the unrestricted Hartree Fock (UHF) method [7] and the restricted open-shell Hartree Fock (ROHF) method [8]. Geometry optimisations using the GAUSSIAN system of programs were performed by the method due to Murtaugh and Sargent [9, 10], while those using the GAMESS system of programs were performed by the method due to Bell et al. [11, 12]. The STO-3G [13] and the 3-21G [14] basis sets were used. All distances quoted are in Ångstrom units (0.1 nm) and all energy values unless otherwise stated are in atomic units (Hartree).

The labelling of the molecule is shown in Fig. 1. The molecule lies in the *yz*-plane, the *z*-axis coinciding with the carbonyl groups.

## 3. Results and discussion

It has been experimentally proven [15] that the two lowest energy triplet states of *p*-benzoquinone are of  $n \rightarrow \pi^*$  type. In fact, the lowest energy singlet state is also produced by an  $n \rightarrow \pi^*$  excitation and the first excited  $\pi \rightarrow \pi^*$  triplet state is higher in energy than this singlet state.

The five highest energy occupied molecular orbitals with their respective 3-21G basis set orbital energies of the ground state of *p*-benzoquinone are:  $1b_{2g}$

(-0.55348),  $5b_{2u}$  (-0.45788),  $4b_{3g}$  (-0.42820),  $1b_{1g}$  (-0.41756) and  $2b_{3u}$  (-0.40525). The three lowest energy virtual molecular orbitals are:  $2b_{2g}$  (0.01143),  $1a_u$  (0.13953) and  $3b_{3u}$  (0.20082). Of these eight molecular orbitals, the  $5b_{2u}$  and the  $4b_{3g}$  molecular orbitals are mainly localised on the oxygen atoms, derived from their  $p_y$  atomic orbitals and referred to as  $n$ -type molecular orbitals; the remainder are  $\pi$ -type molecular orbitals. From purely orbital considerations, it would appear as though there should be two  $\pi \rightarrow \pi^*$  excited triplet states of lower energy than the  $n \rightarrow \pi^*$  excited states shown experimentally to be lower in energy. A survey of previous calculations on  $p$ -benzoquinone shows that the ordering of the five highest energy occupied molecular orbitals is very method dependent. Indeed, the same methodology can produce variations; for instance, using the STO-3G basis set reverses the order of the  $4b_{3g}$  and the  $1b_{1g}$  molecular orbitals. All calculations, however, produce the same ordering of the two  $n$ -type molecular orbitals and show that the higher of the two is more delocalised. This different ordering of the molecular orbitals has given rise to different orderings of the observed ionisation energies. Thus, taking an overview of the calculations, all that can be said is that there are four ionisation potentials in the ten to twelve electron-volt region, two originating from  $\pi$ -type molecular orbitals and two originating from the lone pair molecular orbitals of the oxygens.

Bigelow [16] has published a good description of the molecular orbitals of the ground state of  $p$ -benzoquinone relative to those of isolated benzene and oxygen. He used the CNDO/S method which gives the  $4b_{3g}$  molecular orbital as the highest occupied molecular orbital giving the  $n \rightarrow \pi^*$  excitation the lowest energy. This is in common with the results of Bunce et al. [17] who used the Virtual Orbital Configuration Interaction method within the INDO approximation. Both of these calculations were performed with the crystal structure of the ground state of  $p$ -benzoquinone reported by Trotter [18] for all the states studied.

There have been a number of previous *ab initio* calculations on  $p$ -benzoquinone. Wood [19] investigated the excitation energy to many states using the STO-4G basis set. This basis set produced the same ordering of the molecular orbitals as our STO-3G basis set calculations, the highest occupied molecular orbital being of  $\pi$ -type. Both with and without CI the lowest energy triplet state was shown to be  ${}^3B_{1u}$  ( $\pi \rightarrow \pi^*$ ) with the two  $n \rightarrow \pi^*$  triplet states being at higher energy. They showed, however, that CI brought their excitation energies very close to the experimentally available values. Their calculations were restricted to the full  $D_{2h}$  symmetry of the ground state of the molecule.

Jonkman et al. [20] have done a similar study at the SCF level. They used a [6, 3/3]  $\rightarrow$  (3, 2/2) contracted Gaussian basis set which gave an energy for the ground state of  $p$ -benzoquinone of -378.39209 au, much lower than our 3-21G basis set value of -377.10067 au. They suggested that the  $n$ -type molecular orbitals could be transformed into a lone pair of localised molecular orbitals. Although in the ground state there is no physical difference between the localised and delocalised representations, there should be a large difference when states are considered which involve excitations from these  $n$ -type molecular orbitals. They further reasoned that calculations in which the symmetry imposed on the

molecular orbitals was lowered from the full  $D_{2h}$  symmetry of the ground state to  $C_{2v}$  symmetry should yield such inequivalent localised  $n$ -type molecular orbitals and so the  $n \rightarrow \pi^*$  excitation energy should be lowered. Their molecular orbital ordering was the same as that produced by our 3-21G basis set calculations, and they indeed showed that despite their  $\Delta$ SCF  $D_{2h}$  symmetry excitations giving the  $\pi \rightarrow \pi^*$  excitation a lower energy than the  $n \rightarrow \pi^*$  excitation, their  $\Delta$ SCF  $C_{2v}$  symmetry calculations gave the  $n \rightarrow \pi^*$  excitation the lower energy.

More recently Martin [21] has investigated the same problem. He used Dunning's contraction of Huzinaga's double zeta Gaussian basis set,  $[9, 5/4] \rightarrow (3, 2/2)$ . His ground state energy was  $-379.11435$  au from a projected-broken-symmetry valence bond wavefunction. This value is 2 au lower than our 3-21G basis set energy and even lower than the  $-379.03007$  au produced by a calculation at the 3-21G basis set optimum geometry with a  $[9, 5/6] \rightarrow (4, 2/2)$  contracted Gaussian basis set within the molecular orbital approximation. He reported results for the  $n \rightarrow \pi^*$  excitations only and showed that the broken-symmetry treatment was required to produce excitation energies close to those of experiment. In a subsequent article, Martin and Wadt [22] compared these valence bond results with those from symmetry-restricted CI calculations. They showed that CI was required to bring the excitation energies close to those from experiment.

Finally, Ha [23] has investigated not only the ground and excited states of  $p$ -benzoquinone, but also many of its ionised states. He used a double zeta Gaussian basis set with extensive CI. His molecular orbital ordering was the same as from our 3-21G basis set calculations; and the resultant SCF energy of  $-379.11616$  au was further reduced to  $-379.33202$  au when CI was included. This  $\pi \rightarrow \pi^*$  triplet state was shown to have a lower energy than the  $n \rightarrow \pi^*$  triplet states, but in contrast to the findings of Wood [19], this was reversed on the addition of CI.

One thing in common with all the previous theoretical studies on  $p$ -benzoquinone is that the crystal structure of Trotter [18] or the electron diffraction structure of Hagen and Hedberg [24] was used for both the ground and excited state calculations. This we have shown, from our studies on glyoxal and methylglyoxal [25], to be unsatisfactory, as large changes in geometry can occur. Thus, we have optimised the geometries of the ground state and two excited triplet states ( $A^3B_{1g}$  and  $^3B_{1u}$ ) of  $p$ -benzoquinone; both when the triplet states were constrained to have  $D_{2h}$  symmetry and when the symmetry was relaxed to  $C_{2v}$ .

The calculated 3-21G basis set geometry (bond lengths and bond angles) for the ground state is shown in Table 1, along with the experimental geometry of Trotter [18] for comparison. The molecule is planar so that all dihedral angles are either  $0^\circ$  or  $180^\circ$ . In order to save space, STO-3G basis set geometries will not be reported. This calculated geometry is very close to the experimental geometry: bond lengths differing by no more than  $0.008 \text{ \AA}$  and bond angles by no more than  $1.65^\circ$ . The STO-3G basis set geometry, however, is a little further from the experimental geometry with bond lengths differing by as much as  $0.035 \text{ \AA}$  and bond angles by  $2.2^\circ$ . This geometry is still very reasonable, though, when the

Table 1. Optimised geometries for the ground and two excited triplet states of *p*-benzoquinone, as calculated with the 3-21G basis set<sup>a</sup>

Exp	RHF	ROHF	UHF	ROHF	ROHF	UHF	UHF
<sup>1</sup> A <sub>g</sub> G.S.	<sup>1</sup> A <sub>g</sub> G.S.	<sup>3</sup> B <sub>1u</sub> E.S.	<sup>3</sup> B <sub>1u</sub> E.S.	<sup>3</sup> B <sub>1g</sub> E.S.	<sup>3</sup> B <sub>1g</sub> E.S.	<sup>3</sup> B <sub>1g</sub> E.S.	<sup>3</sup> B <sub>1g</sub> E.S.
D <sub>2h</sub>	D <sub>2h</sub>	D <sub>2h</sub>	D <sub>2h</sub>	D <sub>2h</sub>	D <sub>2h</sub>	D <sub>2h</sub>	C <sub>2v</sub>
C <sub>A</sub> -O <sub>A</sub>	1.222	1.2139	1.3864	1.3805	1.3747	1.3770	1.3801
C <sub>A</sub> -C <sub>C</sub>	1.477	1.4824	1.3834	1.3850	1.3856	1.3857	1.4003
C <sub>C</sub> -H <sub>C</sub>	1.08 <sup>c</sup>	1.0705	1.0695	1.0695	1.0696	1.0692	1.0700
C <sub>B</sub> -O <sub>B</sub>	1.222	1.2139	1.3864	1.3805	1.3747	1.3705	1.3062
C <sub>B</sub> -C <sub>D</sub>	1.477	1.4824	1.3834	1.3850	1.3856	1.3858	1.4214
C <sub>D</sub> -H <sub>D</sub>	1.08 <sup>c</sup>	1.0705	1.0695	1.0695	1.0696	1.0701	1.0698
C <sub>C</sub> -C <sub>D</sub>	1.322	1.3190	1.3797	1.3804	1.3771	1.3769	1.3832
C <sub>A</sub> -C <sub>C</sub> -C <sub>D</sub>	121.1	121.9207	119.6794	119.7517	119.9250	119.1423	119.5163
C <sub>A</sub> -C <sub>C</sub> -H <sub>C</sub>	119.45 <sup>c</sup>	115.8027	118.9555	118.8981	119.2880	119.7385	119.4682
C <sub>C</sub> -C <sub>A</sub> -C <sub>C</sub>	117.8	116.1586	120.6413	120.4966	120.1500	120.9486	121.0235
C <sub>C</sub> -C <sub>A</sub> -O <sub>A</sub>	121.1	121.9207	119.6794	119.7517	119.9250	119.5257	119.4883
C <sub>B</sub> -C <sub>D</sub> -C <sub>C</sub>	121.1	121.9207	119.6794	119.7517	119.9250	120.6814	120.8799
C <sub>B</sub> -C <sub>D</sub> -H <sub>D</sub>	119.45 <sup>c</sup>	115.8027	118.9555	118.8981	119.2880	118.7875	118.2795
C <sub>D</sub> -C <sub>B</sub> -C <sub>D</sub>	117.8	116.1586	120.6413	120.4966	120.1500	119.4040	118.1841
C <sub>D</sub> -C <sub>B</sub> -O <sub>B</sub>	121.1	121.9207	119.6794	119.7517	119.9250	120.2980	120.9079
Total energy <sup>b</sup>	-377.10067	-377.10067	-377.08053	-377.08557	-377.07711	-377.07731	-377.10260

<sup>a</sup> Bond lengths in Ångstrom units, bond angles in degrees<sup>b</sup> Energy values in atomic units<sup>c</sup> These values were assumed

difference in computational requirements on moving from the STO-3G to the 3-21G basis set is considered. Our 3-21G basis set energy was 0.005 au lower than that reported by Ha [23] with the same basis set but the experimental geometry [18, 24].

The electronic configuration of the  $X^1A_g$  ground state of *p*-benzoquinone as calculated with the 3-21G basis set is:

$$\dots (1b_{3u})^2(8a_g)^2(3b_{3g})^2(1b_{2g})^2(5b_{2u})^2(4b_{3g})^2(1b_{1g})^2(2b_{3u})^2,$$

with the three lowest energy virtual molecular orbitals being  $2b_{2g}$ ,  $1a_u$  and  $3b_{3u}$  respectively. Thus, as mentioned earlier it would be expected from purely orbital considerations that the lowest energy excited state would be produced by the  $2b_{3u} \rightarrow 2b_{2g}$  excitation ( $\pi \rightarrow \pi^*$ ). The electronic configuration of this state ( ${}^3B_{1u}$ ) as calculated with the 3-21G basis set within the ROHF approximation and when the symmetry is constrained to be the full  $D_{2h}$  symmetry of the ground state is:

$$\dots (2b_{3u})^1(3b_{3g})^2(1b_{3u})^2(8a_g)^2(2b_{2g})^1(5b_{2u})^2(4b_{3g})^2(1b_{2g})^2(1b_{1g})^2,$$

with the two lowest energy virtual molecular orbitals being  $1a_u$  and  $3b_{3u}$  respectively. Its geometry is shown in the third column of Table 1. The most obvious difference between this geometry and that of the ground state is the much elongated carbon-oxygen bonds. It is also interesting to see that the carbon-carbon double bonds and the carbon-carbon single bonds are now of almost equal length. There are then corresponding changes in the ring angles which effectively leave the ring with the same overall dimensions: the distance between  $C_A$  and  $C_B$  decreases by only 0.137 Å and the distance between the two  $C_C$ s and the two  $C_D$ s decreases by 0.108 Å.

Despite the  $2b_{3u}$  molecular orbital and the  $2b_{2g}$  virtual molecular orbital of the ground state being fairly evenly distributed over the oxygen atoms and the ring carbon atoms, in this excited state the same molecular orbitals, now both singly occupied, become almost localised on the oxygen atoms. The differences in the composition of these two molecular orbitals can go some way to explaining the differences in the bond lengths of the two states. For instance, an electron has been promoted from a molecular orbital which has no node between the oxygen atoms and their attached carbon atoms to a molecular orbital with such nodes. This results in a lengthening of the carbon-oxygen bonds. The same is true for the two  $C_C$ - $C_D$  bonds which are also elongated. The reverse, however, is true of the two  $C_A$ - $C_C$  and the two  $C_B$ - $C_D$  bonds, where the newly occupied molecular orbital has no nodes between the respective carbon atoms while the originating molecular orbital has. This results in a contraction of these bonds.

The  ${}^3B_{1u}$  excited state retains the full  $D_{2h}$  symmetry of the ground state. Even when the geometry is severely distorted, the geometry optimisation procedure still converges to the reported  $D_{2h}$  symmetrical geometry. The 3-21G basis set optimised geometry of this state as calculated within the UHF approximation is shown in column 4 of Table 1. This geometry is almost the same as that produced

within the ROHF approximation. The resultant UHF electronic configuration is:

$$\begin{aligned} & \dots (3b_{3g}^\alpha)^1 (8a_g^\alpha)^1 (3b_{3g}^\beta)^1 (1b_{3u}^\beta)^1 (8a_g^\beta)^1 (2b_{3u}^\alpha)^1 (5b_{2u}^\alpha)^1 \\ & \quad \times (4b_{3g}^\alpha)^1 (5b_{2u}^\beta)^1 (4b_{3g}^\beta)^1 (1b_{2g}^\beta)^1 \\ & \quad \times (1b_{1g}^\alpha)^1 (1b_{1g}^\beta)^1 (2b_{2g}^\alpha)^1, \end{aligned}$$

with the four lowest energy virtual molecular orbitals being  $2b_{3u}^\beta$ ,  $1a_u^\alpha$ ,  $1a_u^\beta$  and  $2b_{2g}^\beta$  respectively. The two unpaired  $\alpha$  molecular orbitals are the  $2b_{3u}^\alpha$  and the  $2b_{2g}^\alpha$  molecular orbitals giving rise to the  ${}^3B_{1u}$  electronic state. The most obvious difference between the resultant optimised ROHF and UHF wavefunctions is that the unpaired  $\alpha$  molecular orbitals in the UHF case are not localised on the oxygen atoms as they are in the ROHF case, but delocalised over the ring carbon atoms as well, as would be expected of  $\pi$ -type molecular orbitals. Despite this, the overall charges on the atoms produced within the two approximations and shown in Table 2 are virtually identical. It is interesting to see that compared with the charges on the atoms of the ground state, also shown in Table 2, there is less of a charge separation between the atoms; both the positive and the negative charges decreasing in value.

As mentioned earlier, it has been experimentally proven that the two lowest energy triplet states of *p*-benzoquinone are of  $n \rightarrow \pi^*$  type. From purely orbital considerations, we would expect the lowest energy  $n \rightarrow \pi^*$  excited state to be produced by the  $4b_{3g} \rightarrow 2b_{2g}$  excitation. The electronic configuration of this state ( ${}^3B_{1g}$ ) as calculated with the 3-21G basis set within the ROHF approximation and when symmetry is constrained to the full  $D_{2h}$  symmetry of the ground state is:

$$\begin{aligned} & \dots (4b_{3g})^1 (4b_{2u})^2 (7b_{1u})^2 (1b_{3u})^2 (8a_g)^2 (3b_{3g})^2 (2b_{2g})^1 \\ & \quad \times (2b_{3u})^2 (5b_{2u})^2 (1b_{2g})^2 (1b_{1g})^2, \end{aligned}$$

with the two lowest energy virtual molecular orbitals being  $1a_u$  and  $3b_{3u}$  respectively. Its geometry is shown in the fifth column of Table 1. This geometry is very similar to that of the  ${}^3B_{1u}$  excited state. Again, compared with the ground state geometry, the carbon–oxygen bonds are substantially elongated and the carbon–carbon double bonds and the carbon–carbon single bonds become of almost equal length. There are also corresponding changes in the ring angles which effectively leave the ring with the same overall dimensions: the distance between  $C_A$  and  $C_B$  decreases by 0.127 Å and the distance between the two  $C_C$ s and the two  $C_D$ s decreases by 0.115 Å. In this case, however, the symmetry of the wavefunction has broken. The two singly occupied molecular orbitals are now localised on the oxygen atoms, the  $4b_{3g}$  molecular orbital is localised on  $O_A$ , while the  $2b_{2g}$  molecular orbital is localised on  $O_B$ . It is also interesting to see some of the other higher energy occupied molecular orbitals localising on different ends of the molecule, particularly the other  $n$ -type molecular orbital, the  $5b_{2u}$  molecular orbital, which is localised on the  $O_B$  end of the molecule; mainly on the oxygen atom but there are significant contributions from  $C_B$  and the two  $C_D$  carbon atoms.

Table 2. Population analysis parameters for the ground and two excited triplet states of *p*-benzoquinone, as calculated with the 3-21G basis set

	ROHF ${}^1A_g$ G.S. $D_{2h}$	ROHF E.S. ${}^3B_{1u}$ $D_{2h}$	UHF E.S. ${}^3B_{1u}$ $D_{2h}$	ROHF E.S. ${}^3B_{1g}$ $D_{2h}$	ROHF ${}^3B_{1g}$ ( ${}^3A_2$ ) E.S. $C_{2v}$	UHF E.S. ${}^3B_{1g}$ $D_{2h}$	UHF ${}^3B_{1g}$ ( ${}^3A_2$ ) E.S. $C_{2v}$
Charges on the atoms:							
C <sub>A</sub>	0.498	0.293	0.294	0.357	0.361	0.384	0.328
O <sub>A</sub>	-0.558	-0.405	-0.406	-0.382	-0.381	-0.484	-0.374
C <sub>C</sub>	-0.260	-0.226	-0.226	-0.268	-0.274	-0.239	-0.253
H <sub>C</sub>	0.290	0.282	0.282	0.273	0.275	0.290	0.274
C <sub>B</sub>	0.498	0.293	0.294	0.267	0.263	0.384	0.348
O <sub>B</sub>	-0.558	-0.405	-0.406	-0.423	-0.425	-0.484	-0.464
C <sub>D</sub>	-0.260	-0.226	-0.226	-0.198	-0.192	-0.239	-0.216
H <sub>D</sub>	0.290	0.282	0.282	0.283	0.282	0.290	0.276
Overlap populations:							
C <sub>A</sub> -O <sub>A</sub>	1.072		0.587			0.868	0.435
C <sub>A</sub> -C <sub>C</sub>	0.419		0.671			0.441	0.666
C <sub>C</sub> -H <sub>C</sub>	0.782		0.790			0.798	0.796
C <sub>B</sub> -O <sub>B</sub>	1.072		0.587			0.868	0.752
C <sub>B</sub> -C <sub>D</sub>	0.419		0.671			0.441	0.540
C <sub>D</sub> -H <sub>D</sub>	0.782		0.790			0.798	0.786
C <sub>D</sub> -C <sub>C</sub>	0.496		0.528			0.742	0.559
Dipole moment (Debye)	0.0	0.0	0.0	0.913	0.908	0.0	0.976
( $S^2$ )							
Before annihilation			2.023			2.124	2.617
After annihilation			2.000			2.006	2.224



Breaking the symmetry from  $D_{2h}$  to  $C_{2v}$  reduces the number of different symmetry orbitals by half:  $b_{1u}$  and  $a_g$  orbitals become  $a_1$  orbitals,  $b_{1g}$  and  $a_u$  orbitals become  $a_2$  orbitals,  $b_{3u}$  and  $b_{2g}$  orbitals become  $b_1$  orbitals and  $b_{3g}$  and  $b_{2u}$  orbitals become  $b_2$  orbitals. The two open-shell molecular orbitals are thus the  $4b_1$  and  $9b_2$  molecular orbitals and the electronic state is  $A^3A_2$ . Thus, the electronic configuration under  $C_{2v}$  symmetry of this excited state is:

$$\dots (9b_2)^1(6b_2)^2(14a_1)^2(1b_1)^2(15a_1)^2(7b_2)^2(4b_1)^1(2b_1)^2(8b_2)^2(3b_1)^2(1a_2)^2,$$

with the two lowest energy virtual molecular orbitals being  $2a_2$  and  $5b_1$  respectively. Allowing the geometry to relax to  $C_{2v}$  symmetry leaves the molecular orbital ordering unchanged and results in small changes to the geometry. This geometry is shown in column 6 of Table 1; comparing it with that of the  $D_{2h}$  symmetry constrained geometry shows a very small lengthening of the  $C_A-O_A$  bond by 0.0023 Å and a small contracting of the  $C_B-O_B$  bond by 0.0042 Å. There is also a slight opening of the  $C_C-C_A-C_C$  bond angle and a slight closing of the  $C_D-C_B-C_D$  bond angle. The remaining bond lengths remain virtually identical. This geometry relaxation process gains only 0.00020 au in energy, which is not enough to correct the ordering of the states. The ROHF approximation then, even with symmetry breaking, still gives the  $\pi \rightarrow \pi^*$   ${}^3B_{1u}$  excited state a lower energy than that of the  $n \rightarrow \pi^*$   ${}^3B_{1g}$  excited state.

The 3-21G basis set optimised geometry as calculated within the UHF approximation and when the symmetry was constrained to be the full  $D_{2h}$  symmetry of the ground state is shown in column 7 of Table 1. The resultant UHF electronic configuration is:

$$\dots (8a_g^\beta)^1(1b_{3u}^\beta)^1(3b_{3g}^\beta)^1(5b_{2u}^\alpha)^1(1b_{2g}^\beta)^1(2b_{3u}^\alpha)^1(4b_{3g}^\alpha)^1 \\ \times (1b_{1g}^\alpha)^1(1b_{1g}^\beta)^1(2b_{3u}^\beta)^1(2b_{2g}^\alpha)^1(5b_{2u}^\beta)^1,$$

with the three lowest energy virtual molecular orbitals being  $4b_{3g}^\beta$ ,  $2b_{2g}^\beta$  and  $1a_u^\alpha$  respectively. The two unpaired  $\alpha$  molecular orbitals are the  $4b_{3g}^\alpha$  and  $2b_{2g}^\alpha$  molecular orbitals giving rise to the  $A^3B_{1g}$  electronic state. The geometry is very different from that calculated within the ROHF approximation. In fact the bond lengths are intermediate between those and those of the ground state: the carbon-oxygen bonds are elongated, the carbon-carbon single bonds are contracted and the carbon-carbon double bonds are elongated. The bond angles are closer to those of the ground state than they are to those of this state within the ROHF approximation. In this case, forcing the geometry to be of  $D_{2h}$  symmetry has constrained the wavefunction to be of the same symmetry. The main difference between this (UHF) wavefunction and that calculated within the ROHF approximation is that the open shell molecular orbitals are more delocalised, with significant contributions from the ring carbon atoms. The  $4b_{3g}^\alpha$  molecular orbital is much more delocalised than it was when it was doubly occupied in the ground state. There is a decrease in contribution from the  $p_y$  atomic orbitals of the oxygen atoms being compensated for by an increase in contribution from those of the carbonyl carbon atoms. The other  $n$ -type molecular orbital,  $5b_{2u}^{\alpha/\beta}$ , also shows an increased contribution from the carbonyl carbon atoms but the large contribution from the oxygen atoms is retained, maintaining the  $n$ -type orbital status.

When the symmetry is allowed to relax from  $D_{2h}$  to  $C_{2v}$ , the result is a large change in the geometry which is shown in column 8 of Table 1, and also a large change in the molecular orbitals. The UHF electronic configuration is:

$$\dots (1b_1^\beta)^1 (15a_1^\alpha)^1 (15a_1^\beta)^1 (7b_2^\beta)^1 (8b_2^\alpha)^1 (2b_1^\beta)^1 (3b_1^\alpha)^1 \\ \times (9b_2^\alpha)^1 (8b_2^\beta)^1 (3b_1^\beta)^1 (1a_2^\alpha)^1 (1a_2^\beta)^1 (4b_1^\alpha)^1$$

with the three lowest energy virtual molecular orbitals being  $4b_1^\beta$ ,  $9b_2^\beta$  and  $2a_2^\alpha$  respectively. The geometry has now become more similar to that calculated with the ROHF approximation, although the differences between the two ends of the molecule are much more pronounced. Most notably are the carbon-oxygen bonds which now differ in length by 0.07 Å. The difference between the carbon-carbon-carbon bond angles at the carbonyl groups has almost doubled at nearly 3°. Finally, in the ROHF case, the difference in length between what used to be the carbon-carbon single and the carbon-carbon double bonds of the ground state is less than 0.01 Å; in this case, however, the difference is a little larger at 0.0171 Å for  $C_A-C_D$  and 0.0382 Å for  $C_B-C_D$ .

The molecular orbitals now tend to localise on either end of the molecule. In the case of the  $n$ -type molecular orbitals, the  $8b_2^\alpha$  ( $5b_{2u}^\alpha$  of  $D_{2h}$  symmetry) molecular orbital is evenly distributed over the whole molecule while the  $8b_2^\beta$  ( $5b_{2u}^\beta$  of  $D_{2h}$  symmetry) molecular orbital is, as with the  $8b_2$  doubly occupied molecular orbital in the ROHF case, localised on  $O_B$ . The singly occupied  $9b_2$  ( $4b_{3g}$  of  $D_{2h}$  symmetry) molecular orbital is localised on  $O_A$  within the ROHF approximation. In the case of the UHF approximation, however, only the unoccupied  $9b_2^\beta$  molecular orbital is localised on  $O_A$ , the occupied  $9b_2^\alpha$  molecular orbital is localised on  $O_B$ . This is also the case with the singly occupied  $4b_1$  ( $2b_{2g}$  of  $D_{2h}$  symmetry)  $\pi$ -type molecular orbital: within the ROHF approximation, it is localised on  $O_B$  while in the UHF case, beside the molecular orbital being delocalised over the ring carbon atoms, the occupied  $4b_1^\alpha$  molecular orbital is largely restricted to the  $O_A$  end of the molecule, and it is the unoccupied  $4b_1^\beta$  molecular orbital that is restricted to the  $O_B$  end of the molecule. Localisation is also observed with some of the other  $\pi$ -type molecular orbitals: within the UHF approximation, in the case of the  $1a_2$  ( $1b_{1g}$  of  $D_{2h}$  symmetry) and the  $3b_1$  ( $3b_{3u}$  of  $D_{2h}$  symmetry) molecular orbitals, the  $\alpha$  molecular orbital is mainly localised at the  $O_B$  end of the molecule while the  $\beta$  molecular orbital is mainly localised at the  $O_A$  end of the molecule. Within the ROHF approximation, this is reflected by the  $1a_2$  molecular orbital which is delocalised over the whole molecule, while the  $3b_1$  molecular orbital has a much larger contribution from the  $O_A$  end of the molecule.

In the UHF case, allowing the symmetry to relax to  $C_{2v}$  produces a large fall in energy (0.13020 au). This state now becomes lower in energy than the  ${}^3B_{1u}$  state as shown by experiment. There is, however, a detrimental effect on the value of  $\langle S^2 \rangle$ , as shown in Table 2. For the  $D_{2h}$ -symmetry constrained triplet state, the value after annihilation is very close to 2.0 which is the value expected for a pure triplet state. In the case of the  $C_{2v}$ -symmetry triplet state, however, the value of  $\langle S^2 \rangle$  is substantially greater than 2.0 and even after annihilation there is still a

large contamination from higher multiplicities. The 3-21G basis set values are a great improvement on those calculated with the STO-3G basis set (3.0591 and 2.7740 before and after annihilation respectively), so perhaps an even better basis set would continue this downward fall towards the desired value of 2.0.

In order to clarify the electronic configurations depicted in the text we have presented two orbital energy diagrams. Figure 2 shows the orbital energy diagram

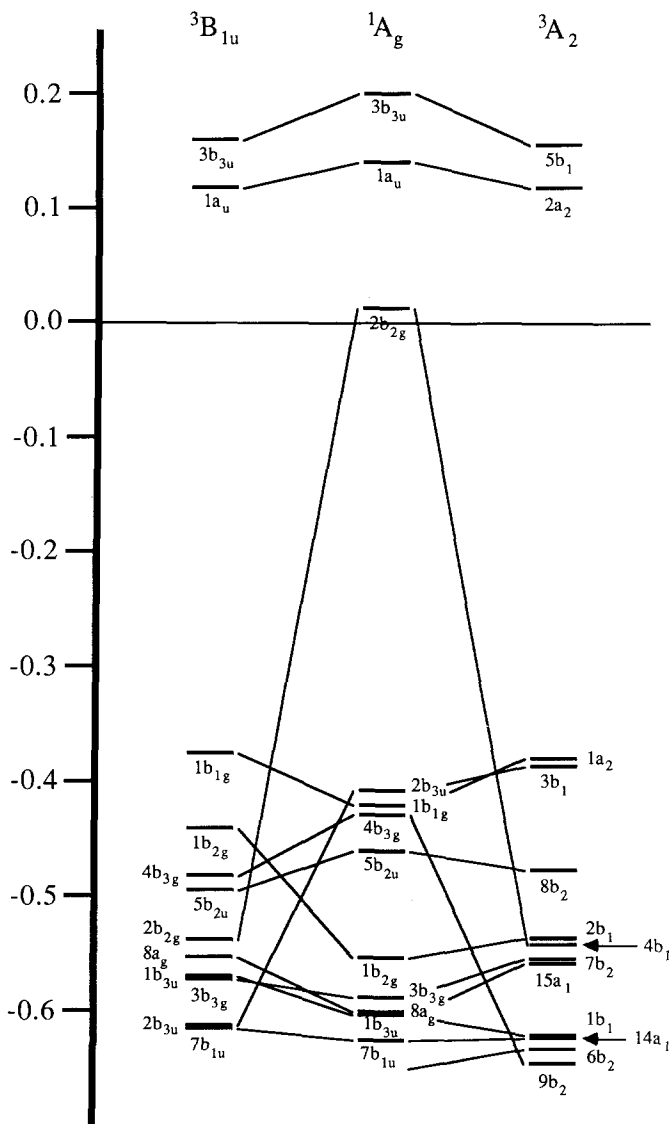


Fig. 2. Orbital energy diagram for the ground state ( $X^1A_g$ ) of *p*-benzoquinone and two of its excited triplet state ( $A^3A_2$  and  $^3B_{1u}$ ); the triplet states being calculated within the ROHF approximation

for the ground state ( $X^1A_g$ ) of *p*-benzoquinone and the two excited triplet states being studied in this work ( $A^3A_2$  and  $^3B_{1u}$ ); the triplet states being calculated within the ROHF approximation. Figure 3 shows the orbital energy diagram for the ground state ( $X^1A_g$ ) of *p*-benzoquinone and these two excited triplet states ( $A^3B_{1g}$  at  $D_{2h}$  symmetry,  $A^3A_2$  at  $C_{2v}$  symmetry and  $^3B_{1u}$ ); the triplet states being calculated within the UHF approximation.

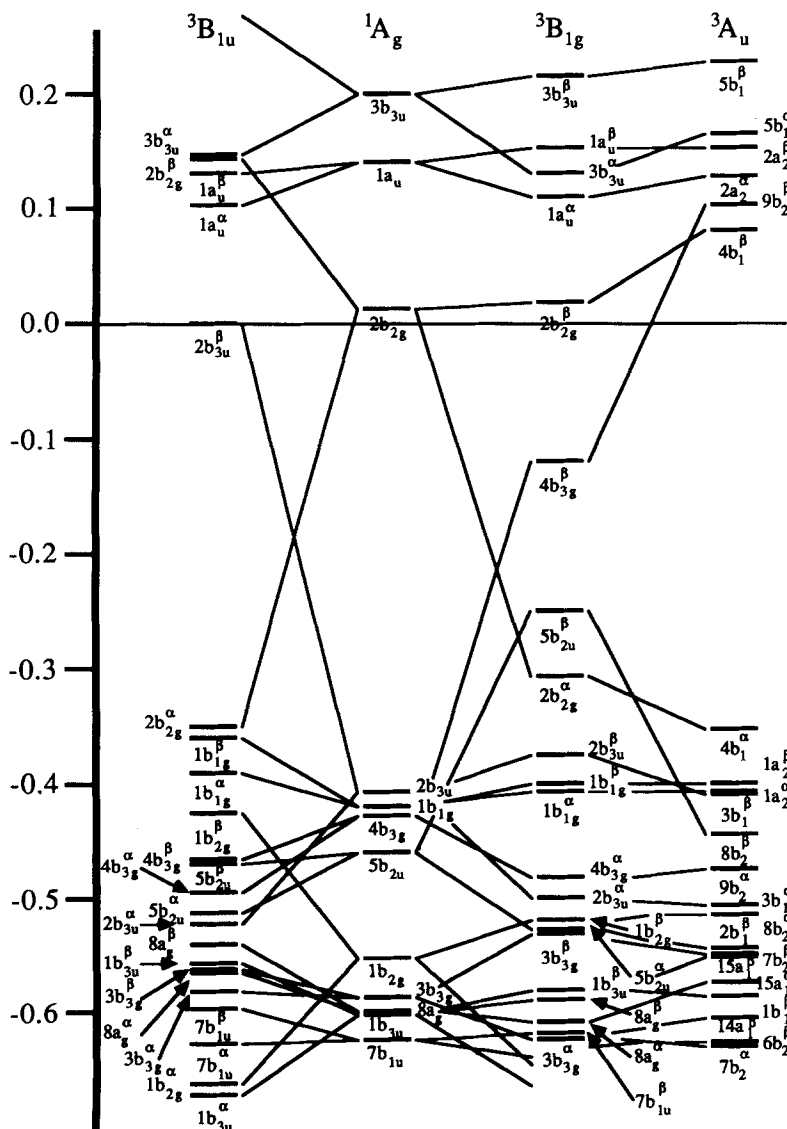


Fig. 3. Orbital energy diagram for the ground state ( $X^1A_g$ ) of *p*-benzoquinone and two of its excited triplet states ( $A^3B_{1g}$  at  $D_{2h}$  symmetry,  $A^3A_2$  at  $C_{2v}$  symmetry and  $^3B_{1u}$ ); the triplet states being calculated within the UHF approximation

#### 4. Conclusion

As our theoretically calculated optimum geometry for the ground state of *p*-benzoquinone is very close to the experimental geometry, there is good reason for using this geometry for investigations on the ground state instead of going to the expense of optimising it. This is particularly shown by the fact that we gained only 0.005 au in energy by optimising the ground state geometry over the value reported by Ha [23] who used the experimental geometry with the same basis set.

In the case of the two triplet states, however, we have again [25] shown the danger of using the ground state geometry, especially when such a delicate quantity as excitation energy is being calculated. Table 1 clearly shows large changes in geometry upon excitation to both the triplet states. These geometry relaxations involve significant energy changes – energy changes which are too large to be neglected.

As our value for  $\langle S^2 \rangle$  from the UHF calculations on the  ${}^3B_{1g}$  excited state is very poor, we might expect the ROHF geometry, with the much smaller difference in the lengths of the carbon-oxygen bonds, to be more reliable. This geometry requires further investigation with more sophisticated techniques. We are presently carrying out such an investigation and hope to report further results in the near future.

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